

Peculiarity of the Coulombic Criticality ?

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We indicate that Coulombic systems could correspond to Wilson effective Hamiltonians similar to that of the ordinary (nonionic) fluids but with a negative φ^4 -coefficient. In that case, solving the “exact” renormalization group equation in the local potential approximation, we show that close initial Hamiltonians may lead either to a first order transition or to an Ising-like critical behavior, the partition being formed by the tri-critical surface. Hence the theoretical wavering encountered in the literature concerning the nature of the Coulombic criticality may not appear senseless.

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In a number of experimental, theoretical and computer simulation studies, the problem of Coulombic criticality has been addressed [1]. For some ionic fluids mean field critical behavior is observed experimentally. Other systems demonstrate Ising-type behavior, while still other ionic fluids exhibit a crossover from classical behavior to Ising-like as the critical point is approached. At the theoretical level, the confused state of the subject has been well described and clarified by Fisher and Stell [1].

Coulombic criticality may be studied within the restricted primitive model (RPM: equal numbers N_+ and N_- of positive and negative hard spheres of equal diameter, d , with charges, $\pm ze$, immersed in a structureless solvent of dielectric permittivity ϵ ; $z/\epsilon = 1$ in what follows). If one generally agrees on the existence of a liquid-gas-like transition at low concentration and low temperature in RPM, it is still not evident what kind of critical behavior the model actually possesses. Mean-field-like or Ising-like critical behavior, crossover from mean-field to Ising behavior, tricriticality or first order transition: all these conclusions have been expressed and discussed [1].

Our aim, in this letter, is first to compute the Wilson effective Hamiltonian corresponding to RPM at its critical point and then to apply the renormalization group (RG) techniques to study it. Let us summarize the main lines of the calculation of the effective Hamiltonian: the details will be published elsewhere [2].

The Hamiltonian of the RPM (in units of $k_B T$) is a sum of the repulsive (hard-core) part and of the coulombic part:

$$H = \frac{\beta}{2} \sum_{i,j}' \phi_{hc}(r_{ij}) + \frac{1}{2} \sum_{\vec{k}}' \nu(k) (\rho_{\vec{k}} \rho_{-\vec{k}} - \rho) \quad (1)$$

here $\phi_{hc}(r_{ij})$ are the hard-core interactions, $\{\vec{r}_i\}$ denote coordinates of the $N = N_+ + N_-$ particles, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, and $\rho = N/\Omega$ is the density, where Ω is the volume of the system. The coulombic interactions in Eq.(1) are written in terms of the *charge density* fluctuation amplitudes, $\rho_{\vec{k}} = n_{\vec{k}}^a - n_{\vec{k}}^b$. The latter are expressed in terms of the amplitudes of *density* fluctuations of positive (a), $n_{\vec{k}}^a = \Omega^{-\frac{1}{2}} \sum_{j=1}^{N/2} \exp\{-i\vec{k}\vec{r}_j^a\}$, and negative (b), $n_{\vec{k}}^b = \Omega^{-\frac{1}{2}} \sum_{j=1}^{N/2} \exp\{-i\vec{k}\vec{r}_j^b\}$, particles. In Eq.(1) $\nu(k) \equiv (4\pi e^2/k_B T)/k^2$, and the primes over sums denote that terms with $i = j$ in the first sum and with $\vec{k} = 0$ in the second sum are excluded.

Using the Hubbard-Schofield scheme [3], we map the ionic fluid Hamiltonian into a Wilson effective Hamiltonian similar to that obtained for ordinary (nonionic) fluids [3] which, discarding the derivatives of the field (local potential approximation), has the following form:

$$H = \int d\vec{r} \left[\frac{1}{2} (\nabla \varphi(\vec{r}))^2 + V(\varphi(\vec{r})) \right] \quad (2)$$

with the “potential function”:

$$V(\varphi) = \frac{1}{9\pi^2} \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n)!} u_{2n} \varphi^{2n} \quad (3)$$

where $b^2 = 4\pi(3\pi)^{2/3}\rho^{*1/3}/T^*$ ($\rho^* = \rho d^3$ is the reduced density and $T^* = k_B T d^3/e^2$ is the reduced temperature). As for the ordinary fluid [3], the coefficients u_{2n} may be expressed in terms of the cumulant averages, $\langle \rho_{\vec{k}_1} \cdots \rho_{\vec{k}_n} \rangle_{cR}$, where averaging is performed over the reference system having only hard-core interactions. First we calculate these quantities for the *lattice-gas* model and find that $u_{2n} = (-1)^{n+1}$ which yield the usual Sine-Gordon Hamiltonian for the RPM [4]. To perform evaluation of the *off-lattice* coefficients u_{2n} we use a symmetry of the RPM with respect to the hard-core interactions, the definitions for the correlation functions, [5,6], and express the coefficients in terms of the Fourier transforms (taken at zero wave-vectors) of the “cluster” functions of the reference hard-sphere system. In obvious notations [6] these read: $h_2(1,2) \equiv g_2(1,2) - 1$, $h_3(1,2,3) \equiv g_3(1,2,3) - g_2(1,2) - g_2(1,3) - g_2(2,3) + 2$, etc., where $g_n(1, \dots, n)$ are n -particle correlation functions. Using the relation between the g_{n+1} and g_n [6],

$$\chi \rho^2 \frac{\partial}{\partial \rho} \rho^n g_n = \beta \rho^l \left[n g_n + \rho \int d\vec{r}_{n+1} (g_{n+1} - g_n) \right], \quad (4)$$

where $\chi = \rho^{-1} \partial \rho / \partial P$ is the compressibility, we iteratively express the Fourier transforms of h_n at zero wave-vectors, $\tilde{h}_n(\vec{0})$, in terms of $\tilde{h}_{n-1}(\vec{0})$ and its density derivative, and ultimately in terms of $\tilde{h}_2(0)$ and its density derivatives. Then we use the relation [6] $\rho \tilde{h}_2(0) = \rho k_B T \chi - 1 \equiv z_0$, and obtain coefficients for the *off-lattice* effective Hamiltonian. In particular, $u_2 = 1$, $u_4 = -(1 + 3z_0)$, $u_6 = 1 + 15(z_0^2 + z_0 z_1 + z_1)$, \dots where $z_1 \equiv \rho (\partial z_0 / \partial \rho)$, \dots . To obtain z_0 one can use the virial expansion for the hard-sphere pressure, $P/\rho k_B T = 1 + \sum_k B_k \rho^k$ with the coefficients B_1, \dots, B_6 known [5] (for small densities), or the Carnahan-Starling equation of state [5,6]. Therefore, applying the above scheme, *all* the coefficients of the effective potential $V(\varphi)$ may in principle be found.

We have studied the density dependence of u_{2n} up to $2n = 14$ and observed that all the coefficients are *negative* in the density interval $\sim 0.07 \sim 0.09$ where the critical density of the RPM is expected to be. We have then performed an *empirical* analysis and found that the boundaries of the density interval where the coefficients u_{2n} are negative depend fairly linearly on $1/n$ (see Fig. 1). Extrapolating this dependence we have found that all the coefficients become *positive* for $n > 22$ (see Fig. 1). Being secure in the knowledge that the effective Hamiltonian is bounded from below, we can envisage a RG analysis.

We thus consider the “exact” RG equation in the local potential approximation [7] in three dimensions which, using the same notations as in [8], reads:

$$\dot{f} = \frac{1}{4\pi^2} \frac{f''}{1+f'} - \frac{1}{2} y f' + \frac{5}{2} f \quad (5)$$

in which y stands for the dimensionless field and $f(y, l) = \partial V(y, l) / \partial y$, $f' = \partial f / \partial y$, $f'' = \partial^2 f / \partial y^2$, $\dot{f} = \partial f / \partial l$ with l the RG scale parameter (that relates two different “momentum” scales of reference such that $\Lambda_l = e^{-l} \Lambda_0$).

Ideally, the question raised may be formulated as follows: considering the effective Hamiltonian for the RPM at its assumed critical point (taken e.g. from Monte Carlo data [9,10]) as an initial Hamiltonian ($l = 0$) for Eq. (5), will the solution of Eq. (5) flow toward the Ising fixed point [the unique non-trivial fixed point of Eq.(5)] or not?

Unfortunately, considering the function $f(l = 0, y)$ which gives the initial conditions of RPM for Eq.(5) (at $\rho_c^* = 0.0857$, $T_c^* = 0.052$ [9], or $\rho_c^* = 0.080$, $T_c^* = 0.0488$ [10]), we have observed that the denominator $1 + f'(y)$ in (5) has singularities in the interval, $0.1 < y < 0.12$. Moreover, Eq.(5) does not allow us to handle values of Hamiltonian coefficients as large as those of Eq.(3). Considering that Eq. (5) is an approximation, that impossibility has no particular significance relative to the behavior of RPM.

However, we have considered that the negative value of u_4 found for RPM could be a characteristic feature of qualitative importance for (some) ionic systems. Thus we turn our attention to the solutions of Eq.(5) with initial functions involving negative values of u_4 .

In [8] a detailed study of the approach to the Ising fixed point using Eq. (5) has been presented. However all the initial Hamiltonians considered were taken with $u_4 > 0$. To our knowledge, the few studies based on RG techniques that have, up to now, considered negative values of u_4 , either perturbatively [11] in three dimensions or, more recently, non-perturbatively [12] in four dimensions, have concluded that there is no stable fixed point (the Ising fixed point cannot be reached starting with $u_4 < 0$) and thus to the lack of “true” criticality (there would be no divergent correlation length, like in a first order transition).

To be short, we consider the following simple functions as initial conditions to Eq. (5) (a detailed study of the case $u_4 < 0$ will be published elsewhere [13]):

$$f(y, 0) = u_2(0)y + u_4(0)y^3 + u_6(0)y^5 \quad (6)$$

corresponding to a point of coordinates $(u_2(0), u_4(0), u_6(0), 0, 0, \dots)$ in the space \mathcal{S} of Hamiltonian coefficients (the dimension of \mathcal{S} is infinite). Since we want to set $u_4(0) < 0$, and at least one positive higher term is needed to make

the Hamiltonian bounded from below, we choose to set $u_6(0)$ positive. Having chosen a (negative) value for $u_4(0)$ and a (positive) value for $u_6(0)$, we use the “shooting” method [8] to determine the critical value $u_2^c(0)$ of $u_2(0)$ which brings $f(y, 0)$ in the critical subspace \mathcal{S}_c of \mathcal{S} . The “shooting” method is based on the fact that, for sufficiently large values of l , the RG trajectories go away from \mathcal{S}_c in two opposite directions according to the sign of $u_2(0) - u_2^c(0)$.

Let us summarize our results by considering the case $u_4(0) = -6$ as an example (see Fig. 2).

- A If $u_6(0) = 16$, we find $0.3836174 > u_2^c(0) > 0.3836151$. The associated RG trajectory goes away from the Gaussian fixed point P_G and remains in the sector $u_4 < 0$ of \mathcal{S}_c . Hence it never reaches the Ising fixed point that lies in the sector $u_4 > 0$. Instead the trajectory is attracted to a stable submanifold of dimension one (an infra-red stable trajectory) that emerges from P_G . On a pure field theoretical point of view, this trajectory is a *renormalized* trajectory (let us denote it by $T_{u_4 < 0}$) to which is associated the continuum limit of an asymptotically free scalar field theory in three dimensions. It is very likely that $T_{u_4 < 0}$ is the continuation below four dimensions of the continuum limit recently studied on a lattice in [12] and corresponding to a scalar theory with negative quartic interaction. *The lack of any fixed point ending $T_{u_4 < 0}$ means that the correlation length remains finite at the assumed critical point.* This situation could be compared to the fact that no heat-capacity divergency has been observed in the Monte Carlo study of the RPM [9].
- B If $u_6(0) = 20$, we find $0.30131 > u_2^c(0) > 0.30122$ and the associated RG trajectory goes toward the (Wilson–Fisher) Ising fixed point and approaches it along the usual renormalized trajectory associated with the continuum limit of the scalar field theory in three dimension usually called the φ_3^4 -field theory. This renormalized trajectory (denoted by T_1 in [8]) interpolates between the Gaussian and the Ising fixed points. Hence *there exist initial Hamiltonians with $u_4 < 0$ that belong, nevertheless, to the basin of attraction of the Ising-like fixed point.*
- C Between the two preceding cases, we find a trajectory (with $u_6(0) = 18.3125 \dots$ and $0.3324573 > u_2^c(0) > 0.3324549$) that directly flows towards P_G (it is neither attracted to $T_{u_4 < 0}$ nor to T_1). That kind of initial Hamiltonian obtained by adjusting two coefficients ($u_2(0)$ and $u_6(0)$) lies on the *tri-critical subspace* \mathcal{S}_t of \mathcal{S} . Any trajectory on \mathcal{S}_t approaches P_G along a unique (attractive) trajectory that imposes the required very slow (logarithmic) flow in the vicinity of P_G (see Fig. 2).

So, it appears that for $u_4(0) < 0$, very close Hamiltonians may lead to very different behaviors and this feature is due to the vicinity of the tricritical subspace. If one adopts the idea that effective Hamiltonians for Coulombic systems may be characterized by a negative value of u_4 , then it is not amazing that the tricritical state has been the center of a recent discussion relative to the nature of the Coulombic criticality. Also, it is easy to verify that the experimental observations of mean field values for the critical indices might be due to a retarded crossover towards the Ising behavior [14]. One may observe on Fig. 2 that the trajectory corresponding to case B follows a long path to the Ising fixed point (and passes close to P_G) compared to a trajectory that could correspond to a simple fluid. In order to illustrate qualitatively that retarded crossover, we have drawn in Fig. 3 the evolutions [calculated from Eq. (5)] of a pseudo effective exponent $\nu_{\text{eff}}(\tau = |u_2(0) - u_2^c|/|u_2^c|)$ associated to two effective Hamiltonians with $u_4(0) = -6$ and $u_6(0) = 20$ on one hand [RPM-like ? (B)] and $u_4(0) = +3$ and $u_6(0) = 0$ on the other hand (Simple fluid).

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- [1] Experimental reviews: K. S. Pitzer, Acc. Chem. Res. **23**, 333 (1990); J. M. H. Levelt-Sengers and J. A. Given, Molecular Phys. **80**, 899 (1993); H. Weingärtner, M. Kleemeier, S. Wiegand and W. Schröer, J. Stat. Phys. **78**, 169 (1995); H. Weingärtner and W. Schröer, J. Mol. Liq. **65-66**, 107 (1995). Theoretical reviews: M. E. Fisher, J. Sta. Phys. **75**, 1 (1994); J. Phys.: Cond. Matt., **8**, 9103 (1996); G. Stell, J. Phys.: Cond. Matt., **8**, 9329 (1996); J.Stat.Phys., **78**, 197 (1995).
 - [2] N. V. Brilliantov, J. P. Valleau, in preparation.
 - [3] J. Hubbard and P. Schofield, Phys. Lett., **A40**, 245 (1972).
 - [4] H. Kleinert, *Gauge Fields in Condensed Matter*, World Sci., Singapore, 1989, v.1, Chap.7. Some (unimportant) difference of our result occurs because the present calculations are performed for the canonical ensemble.
 - [5] J. A. Barker and D. Henderson, Rev. Mod. Phys., **48**, 587 (1976).
 - [6] C. G. Gray and K. E. Gubbins, *Theory of molecular fluids*, Clarendon Press, Oxford, 1984.
 - [7] A. Hasenfratz and P. Hasenfratz, Nucl. Phys. **B270 [FS16]**, 687 (1986).
 - [8] C. Bagnuls and C. Bervillier, J. Phys. Stud. **1**, 366 (1997); see also Phys. Rev. **B41**, 402 (1990).

- [9] J. P.Valleau and G. M.Torrie, in preparation.
- [10] J. M.Caillol, D. Levesque and J. J. Weis, J. Chem. Phys., to appear
- [11] E. K.Riedel and F. J. Wegner, Phys. Rev. Lett., **29**, 349 (1972); Phys. Rev. **B9**, 294 (1974); A. I.Sokolov, Sov. Phys. JETP, **50**, 802 (1979).
- [12] K. Langfeld and H. Reinhardt, hep-ph/9702271, submitted to Phys. Lett. B.
- [13] C. Bagnuls and C. Bervillier, in preparation.
- [14] See M. E. Fisher in [1] and references therein.

FIGURE CAPTIONS

Figure 1 Dependence of the boundaries of the density interval where the coefficients u_{2n} of the effective Hamiltonian are negative as a function of $1/n$. Extrapolation suggests that *all* the coefficients with $n > 22$ are positive. (Note that the density at which the “negative” interval shrinks to zero, $\rho = 0.0856$ is very close to the critical density from the Monte Carlo data [9,10]).

Figure 2 Projection onto the plane $\{u_2, u_4\}$ of various RG trajectories (in \mathcal{S}_c) obtained by solving Eq. (5). Black circles represent the Gaussian (P_G) and Ising (IFP) fixed points. The ideal trajectory (dot line) which interpolates between these two fixed points represents the renormalized trajectory (RT) of the so-called ϕ_3^4 field theory in three dimensions (usual RT). White circles represent the projections onto the plane of initial (unrenormalized) critical Hamiltonians. For $u_4(0) > 0$, some effective Hamiltonians run toward the Ising fixed point asymptotically along the usual RT (simple fluid). Instead, for $u_4(0) < 0$ and according to the values of Hamiltonian coefficients of higher order, the RG trajectories either (A) meet an endless RT emerging from P_G (dashed curve) and lying entirely in the sector $u_4 < 0$ or (B) meet the usual RT towards IFP. The frontier which separates these two very different cases (A and B) corresponds to initial Hamiltonians lying on the tri-critical subspace (white square C) that are source of RG trajectories flowing toward the P_G asymptotically along the tricritical RT. Notice that the coincidence of the initial point B with the RG trajectory starting at point A is not real (it is accidentally due to the projection onto a plane). The restricted primitive model could correspond either to the case A or to the case B.

Figure 3 Sketchy representation of the effective exponents $\nu_{\text{eff}}(\tau)$ calculated in the local potential approximation along the two RG trajectories which, on Fig. 2, both flow towards the Ising fixed point [“RPM-like ? (B)” corresponds to $u_4(0) < 0$ and “Simple fluid” to $u_4(0) > 0$]. The full lines roughly indicate the experimentally accessible parts in each case.





